Photocatalytic Activity of Commercial TiO_2 Oxides in the Oxidation Reaction of Nitric Oxide

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ABSTRACT

In this work, five commercial titanium oxides, R-706 from DUPONT™, P-25 from DEGUSSA™, BLR-699 from YUEJIANG™, RC-8640A and RC-8640B from RUI-CHEM™ were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS) and nitrogen adsorption-desorption isotherms (BET), and its photocatalytic activity was tested in the oxidation reaction of nitric oxide (NO). The conversion degree (%) of NO reached by each oxide was associated with their physical properties such as crystalline structure, specific surface area, and particle size. In the same way, the effect of the charge of photocatalyst was also studied.

***Keywords*:** TiO_2, photocatalysis, NO_x

1 INTRODUCTION

Nowadays, the interest by the development of sustainable materials for construction applications is increasing due to the importance to preserve the environment. Undoubtedly, one of the most interesting technologies focused in this direction is the heterogeneous photocatalysis, where the solar radiation is used by a semiconductor oxide for induce the elimination of a great variety of pollutants [1]. By far, the anatase polymorph of TiO_2 is the photocatalyst of excellence for commercial applications because of its high activity under UV irradiation, and stability to corrosion processes [2]. On the other hand, although rutile polymorph of titanium oxide has a lower activity, the combination of both polymorphs can produce a material with synergistic photocatalytic properties as the well-known TiO_2 P-25 (Degussa).

For these reasons, will be explored the potential application of five commercial titanium oxides with different crystalline structures to act as an efficient photocatalyst in the conversion oxidation reaction of NO_x gases to innocuous products as nitrites or nitrates. The generic term NO_x refers to a group of oxides formed by the chemical combination of nitrogen and oxygen in different ratios ($NO + NO_2$) and constitutes one of the most common air pollutants. This topic is of particular relevance in big cities where the accumulation of NO_x compounds in the air represents a serious problem. For example, nitrogen oxides (NO_x) are the origin of various health and environmental problems, such as irritated eyes, headache, pulmonary emphysema, acid rain, acidification of aquatic systems, ozone depletion, and photochemical smog [3]. Among the various proposed technologies to solve this problem, the heterogeneous photocatalysis has received an increasing interest in recent years [4-5].

2 EXPERIMENTAL

The commercial oxides R-706 from DUPONT™, P-25 from DEGUSSA™, BLR-699 from YUEJIANG™, RC-8640A and RC-8640B from RUI-CHEM™ were supplied by the company Pinturas Térmicas del Norte. The samples of commercial TiO_2 oxides were analyzed as were received without a further treatment. The structural characterization of TiO_2 samples was carried out by X-ray powder diffraction using a D8 Advance diffractometer with Cu Ka radiation. Diffraction experiments were performed with a step size of 0.05^o and a dwell time of 0.5 s. The morphology and particle size of the samples were analyzed by scanning electron microscopy by using a FEI Nova NanoSEM 200 microscope with an accelerating voltage of 30 kV. The UV-Vis diffuse reflectance absorption spectra of the samples were obtained by using an UV-Vis

spectrophotometer PerkineElmer Lambda 35 equipped with an integrating sphere. The BET surface area measurements were carried out by N_2 adsorption/desorption isotherms by means of a Bel-Japan Minisorp II surface area and pore size analyzer. The isotherms were evaluated at -196°C after a pretreatment of the samples at 150°C for 24 h.

The photocatalytic activity of TiO_2 samples was evaluated by the removal of nitric oxide from air under UV irradiation. The photocatalytic experiments were carried out in a laboratory test set-up designed according with the standard ISO 22197-1:2007 as is shown in Figure 1. The photocatalytic reactor was made of stainless steel with a volume of 0.8 L. The device has integrated a window made of tempered glass in its superior part in order to allow the pass of radiation. The photocatalyst (200 mg) dispersed previously in ethanol was deposited over an area of 0.08 m^2 in a glass substrate with the help of a small brush. As inlet gas was used a mixture 3 ppm of NO stabilized in N_2. The concentration of gas was adjusted to 1 ppm in NO by using air and the flow rate of gas was adjusted to 1 $L \cdot min^{-1}$.

The source of light irradiation were two fluorescent black lamps (TecnoLite) of 20 W each one emitting between 365 and 440 nm The main contribution of the radiation source comes from the emission line at 365 nm, and, in minor proportion from two emission lines located in the visible region at 405 and 437 nm. The concentration of nitric oxide was continuously measured with a chemiluminescent NO_x analyzer (EcoPhysics CLD88p) with a sampling rate of 0.3 $L \cdot min^{-1}$.

3 RESULTS AND DISCUSSIONS

Figure 2 shows the X-ray diffraction pattern of the five commercial oxides. In the samples identified as R-706 and BLR-699, the main diffraction lines were associated with the rutile structure type of TIO_2 in agreement with the JCPDS Card No. 1-1292. Additionally, the diffractogram of the sample R-706 showed the presence of ZnO in a minor proportion (JCPDS 36-1451). In the same way, TiO_2 anatase oxide was also detected in the sample BLR-699.

As is well known, the oxide usually used as reference in photocatalytic experiements (P-25), is constituted by a mixture of anatase and rutile polymorphs of TiO_2 approximately in a proportion of 70-30 % of each oxide, respectively.

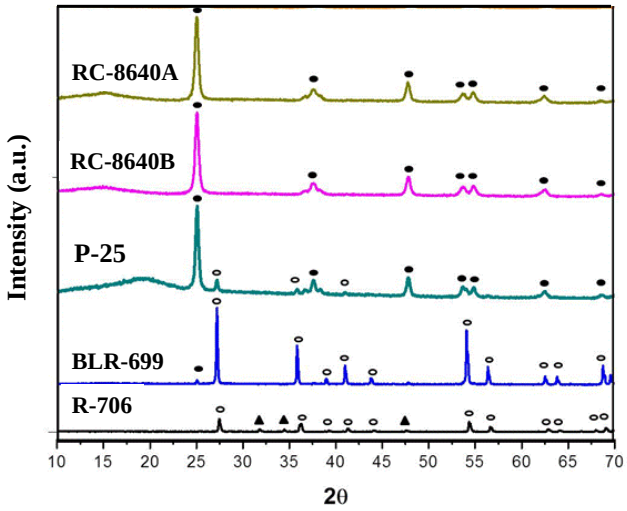

Figure 2. X-ray diffraction patterns of commercial TiO_2. (o) rutile, (●) anatase, and (▲) ZnO.

In the sample RC-8640A and RC-8640B only were detected diffraction lines associated with the anatase polymorph of TiO_2. In general, the crystallinity of the commercial oxides was decreasing in the follow order; RC-864040A > RC-8640B > P-25 > BLR-699 > R-706.

The analysis of commercial oxides by SEM revealed materials with an average of size particle of 250-300 nm (BLR-699), 350-550 nm (R-706), < 50 nm (P-25), and < 50 nm (RC-8640A and RC-8640B). As a characteristic property, large agglomerates of primary particles were observed in R-706 whose dimensions were about 3 μm.

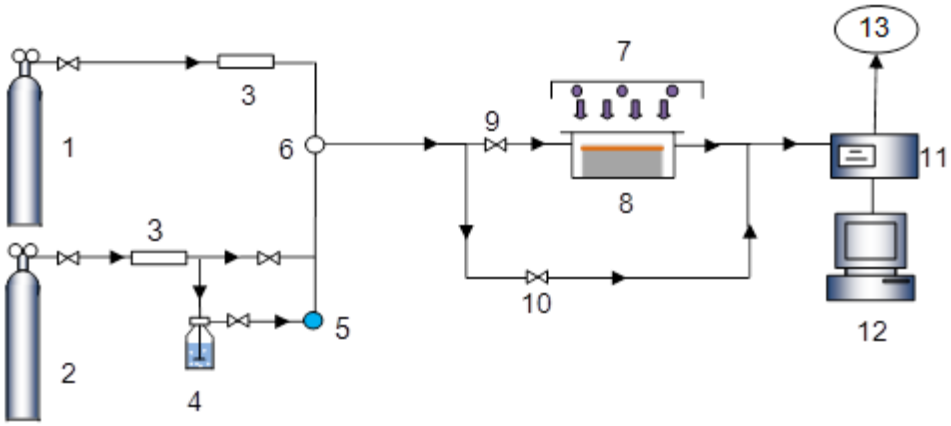

Figure 1. Schematic diagram of the photocatalytic degradation set-up. 1. NO gas supply; 2. Synthetic air; 3. Mass controller meter; 4. Humidifier; 5. Humidity controller; 6. Temperature and relative humidity sensor; 7. Light source; 8. Reactor; 9. Valve; 10. Valve; 11. NO_x analyzer; 12. Computer; 13. Vent.

The specific surface area of samples was determined throughout BET protocol. By an analyses of the profile of the N_2 adsorption/desorption isotherms was concluded that the materials were not porous and has a high energy of adsorption. Table 1 shows the specific surface area calculated for each oxide.

Sample	Surface area (m^2 g^{-1})	Energy band gap (eV)
R-706	10.3	3.0
BLR-699	16.8	3.0
P-25	50.2	3.1
RC-8640A	74.5	3.1
RC-8640B	78.8	3.2

Table 1. Some physical properties of the commercial TiO_2 oxides.

As can be noticed in Table 1, TiO_2 samples present similar energy band gaps values between them. These values were ranging between 3.2 and 3.0 eV which corresponds with the typical values of the TiO_2 for anatase and rutile crystal structures.

The assessment of photocatalytic activity of the oxides was performed in a photocatalytic reactor designed according with the ISO 22197-1. Figure 3 shows the conversion degree (%) of NO reached by each oxide in the course of 60 min of lamp irradiation. For the first 25 min of reaction, the materials where the anatase polymorph was the main phase exhibited the highest photocatalytic activity, i.e. P-25, RC-8640A, and RC-8640B. In fact, the conversion degrees of NO (%) reached at this time values near to 95%. After 25 min of reaction, P-25 and RC-8640A retained almost the 100% of its photocatalytic activity. By the other hand, RC-8640B undergoes an important deactivation process which reduced the conversion degree of NO until a 60% after 60 min of reaction. In a contrary behavior, the samples in which the predominant phase was rutile (R-706 and BLR-699) showed a poor photocatalytic activity. In first instance, the materials were quickly activated but their maximums of conversion degree were reached around 12 minutes, and then a remarkably deactivation process was observed. Among rutile samples, BLR-699 was the best photocatalyst with a conversion degree value of 70% during a short time of reaction.

The crystalline structure was the main factor to condition the photocatalytic activity of the commercial oxides. It is well recognized that the crystalline structure of anatase is more active than the rutile polymorph, mainly due to a better charge transference and the existence of crystalline planes with high photocatalytic activity in the anatase polymorph [6]. Some authors have attributed the high photcatalytic activity of P-25 with a synergistic process between anatase and rutile polymorphs at the specific composition of 70/30 of each oxide.

The specific surface area is a secondary factor to taking into account in the assessment of photocatalytic activity of the commercial TiO_2 oxides. It can be the origin of the different activities observed in the rutile oxides. Due to the amount of mass of photocatalyst used in the experiments, 200 mg dispersed in an area of 0.08 m^2, the adsorption process of the NO molecule over surface of photocatalyst should have a relevant importance. By this cause, the specific surface area of oxides plays an important role in the activity observed. In relation with this physical property, the particle size can has an important influence. In both series of samples, anatase and rutile oxides, the samples

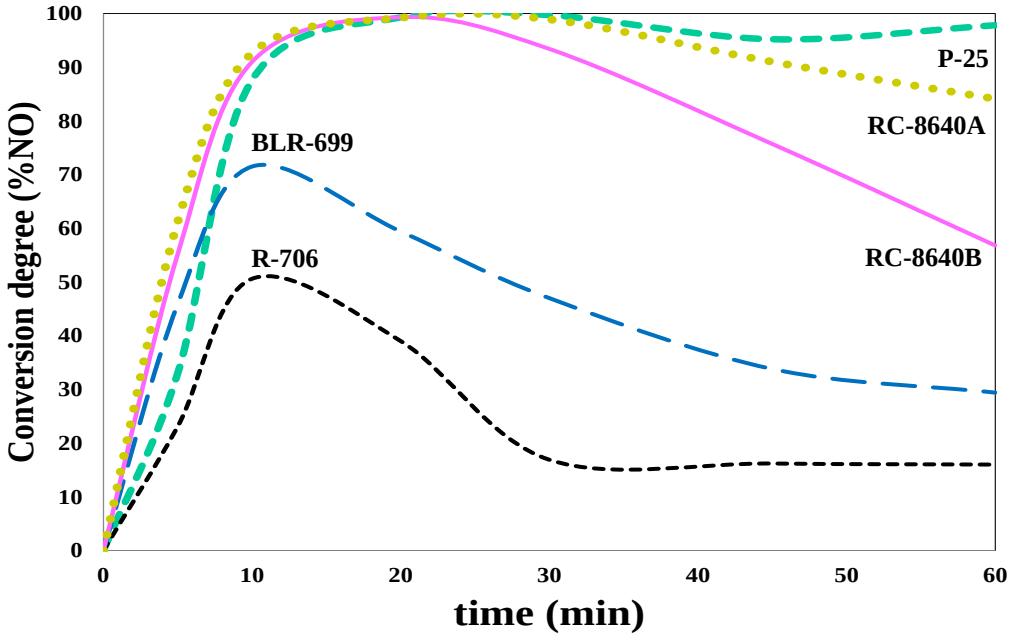

Figure 3. Photocatalytic activity of commercial TiO_2 oxides for NO conversion.

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with particle sizes at lowest nanometric scale exhibited the highest phootcatalytic activity, i.e. P-25 and BLR-699, respectively. In this sense, a small particle size can reduce considerably the pathway to follow by the charges generated (electrons and holes) from its point of generation until the surface of the photocatalyst.

With the purpose of evaluate the activity of the best photocatalyst under more drastic experimental conditions, a series of experiments were performed where the mass of P-25 photocatalyst were reduced to 100 and 50 mg, as is shown in Figure 4. As can be seen, the performance of P-25 was similar when the mass of the oxide was reduced in a 50% (100 mg). Only when the charge of the photocatalyst was reduced in a 75% (50 mg) was appreciable a reduction in the conversion degree of NO in the stationary state, which after 60 min reached a value of 65%.

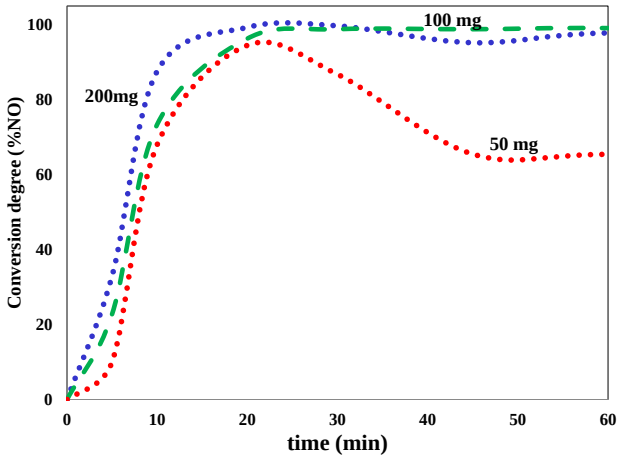

Figure 4. Conversion degrees of NO with different charge of P-25 photocatalyst.

Titanium dioxide can be incorporated as raw material in large applications such as cement, asphalt, ceramic tiles, glass, and paints. Due to these materials are usually applied over surfaces exposed to sun light irradiation, this technology can be considered to the development of new sustainable materials for the industry of construction. In this sense, an important factor to choose the commercial oxide is the cost involved. For example, the costs of R-706, RC-8640A and P-25 per kg are $2.95, $4.40, and $45.0 USD. Over the basis of this parameter, and taking into account its photocatalytic activity, RC-8640 seems to be the most efficient material to be considered for a further technological application. Of course, other parameters must be considered such as the dispersion degree and interaction of TiO_2 oxide with the host matrix.

4. CONCLUSIONS

The conversion degree (%) of NO reached by each oxide was associated with their physical properties such as crystalline structure, specific surface area, and particle size, In the same way, the effect of the charge of photocatalyst was also studied.

Titanium dioxide can be incorporated as raw material in large applications such as cement, asphalt, ceramic tiles, glass, and paints. Taking into account its photocatalytic activity and cost, RC-8640 seems to be the most efficient material to be considered for a further technological application.

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